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Effects of ^{18}O Exchange on Neutron Emission Rates of Aging $^{238}PuO_2$ LWRHUs

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Contents

Figures

Tables

Introduction

The Lightweight Radioisotope Heater Unit (LWRHU) provides about 1 Watt of thermal power to critical electrical and mechanical systems in the extreme temperatures of space, maintaining the operating temperature of the spacecraft's scientific and general operating equipment. Los Alamos National Laboratory (LANL) designed and tested the LWRHU in the 1970s through early 1980s. The first production campaign at LANL was in the early 1980s in support of the Galileo mission in which over 100 LWRHUs were manufactured. In the mid-1990s, almost 200 LWRHUs were manufactured in support of the Cassini mission. After the primary Cassini manufacturing campaign, the Department of Energy (DOE) approved the fabrication of more than 10 additional LWRHUs as spares in 1998.

The LWRHU assembly contains the following components: a fuel pellet, a vented capsule, a pyrolytic graphite insulator, and a fine-weave pierced fabric (FWPF) graphite aeroshell. (Figure 1 contains an exploded view of the LWRHU.) The fuel pellet is a hot-pressed $^{238}PuO_2$ cylindrical pellet that is sintered to create a ceramic pellet. The pellet is encapsulated in a platinum-rhodium encapsulation. The welded fueled clad is placed inside a pyrolytic graphite thermal insulation to protect the fuel from the heat produced in reentry events. The exterior layer of the LWRHU assembly is the FWPF aeroshell.

Before sintering, PuO_2 granules are heated in a furnace at temperatures greater than or equal to 700°C under an enriched ^{16}O atmosphere in order to reduce trace quantities of ^{18}O. Because ^{18}O undergoes an (α,n) reaction, ^{18}O needs to be removed as much as possible to meet radiation emission requirements set by the Jet Propulsion Laboratory (JPL) and the National Aeronautics and Space Administration (NASA), as well as other agencies. The relative abundances of the oxygen isotopes are indicated by neutron emission rate (NER) measurements.

LWRHUs are vented with a sintered platinum frit vent (George 1986). During extraterrestrial operation, the vent in the cladding allows helium from the decay of plutonium to escape and relieves pressure from the system while preventing the solids from escaping (Rinehart 1996, Tate 1982 & 1985). This vent is protected during manufacture by a platinum-30 rhodium cover. The capsule vent is activated by milling a 0.025-inch diameter hole through the protective cover to a nominal depth of 0.015 inches, generally immediately before the LWRHU is loaded into the aeroshell (George 1986). Prior to long-term storage, LWRHUs are vented and thus potentially allow infiltration of ^{18}O from the ambient atmosphere.

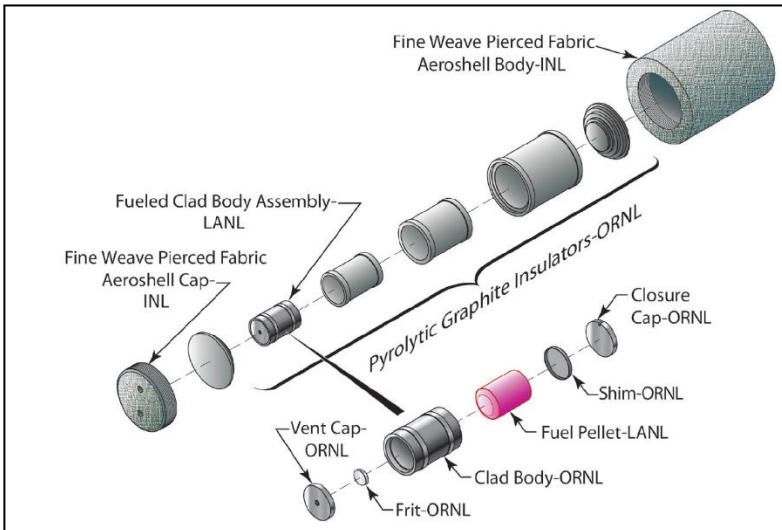

Figure 1. LWRHU Assembly Exploded View.

Although NER decreases with age due to the reduction in emitted alpha particles, it might be expected that NER reduction is mitigated by the exchange of ^{18}O.

However, this is not necessarily the case and no trend was observed relating NER to age other than the natural decay of ^{238}Pu (Mulford 2021). The most probable and dominant factor for determining specific

NER was manufacturing discrepancies between individual units. It is important to understand the lack of observed ^{16}O-^{18}O exchange and to compare LWRHU pellets as much as possible.

Data Presentation

Based on the limited historical and current information available regarding LWHRU NERs, there are initial assumptions that were made, as follows:

1. Diffusion mechanisms at the surface and interior, which can then be subdivided into
    a. Sub- and superstoichiometric oxide formation at the surface ($PuO_{2\pm x}$)
    b. Migration of ^{18}O into the pellet through grain boundaries and not into the Pu-O lattice
2. Sintering produces a pellet that, although between 75% - 90% theoretical density (TD), is almost impermeable to gases heavier than He
3. The kinetics of the exchange are unfavorable at the temperatures the pellet is stored at.

The abundance of the isotopes being exchanged might have some effect, and that is due to the relative abundances, exchange of ^{18}O might be negligible. However, over the course of almost three decades, NER should increase as the pellet's oxygen isotopes come to equilibrium with the atmosphere. Non-stoichiometric oxides is an issue for plutonium metal, and operating under the assumption that the pellet is wholly PuO_2, this can be neglected. Plutonia stoichiometry after hot pressing is $PuO_{1.93}$, but pellets are oxidized back to stoichiometric ratio under a purified Ar-$H_2{}^{16}O$ flow gas before sintering (Rinehart 1988 & 1996).

LWRHU pellets are manufactured to be porous to allow helium diffusion out of the pellet, but it has been reported that if a pellet is sintered prior to undergoing ^{16}O exchange, the exchange will be incomplete even at high temperatures (Miles 1972). For granules at low TD, exchange is complete, so it is important to consider whether or not the sintered pellet is impermeable to ^{18}O. Diffusion of ^{18}O within the pellet needs to be examined. The temperature gradient of the LWRHU pellet drives faster diffusion from the center to the surface. While oxygen point defects have been examined, it is not understood how exactly oxygen migrates within the bulk of the material (Wang 2019). It is not known if incoming ^{18}O travels primarily along grain boundaries and therefore has limited exchange with oxygen in the lattice, but this is only speculative.

Exchange of ^{18}O is conducted at temperatures in excess of 700°C, and, as such, studies have focused on exchange mechanisms at these temperatures (Whiting 2015, Miles 1972, Saltas et al 2017). There is limited information on exchange mechanisms at lower temperature. There are many variables to consider regarding ^{18}O diffusion. First is the amount of ^{18}O in the surrounding air, which is dependent on how the LWRHU is stored. If the LWRHU is in a sealed product can, then there is a very limited reservoir of ^{18}O that can re-exchange. Second is the flow rate of the sintered platinum vent frit. Product specifications indicate that the max flow rate of escaping helium is 0.01-0.03 cm^2/s for a 1 psi differential. Because of the temperature, the pressure differentials within the cladding, and the heavier ^{18}O mass than the helium the frit was designed for, it can be assumed that there is a much lower flow rate back into the frit.

NER change as a function of age

While NER decreases as expected over time as a result of the decay of the ^{238}Pu, no conclusion can be drawn. Figure 1 shows how much the NER differs from what was expected due to decay. The NER values from ^{238}Pu samples at 25.5 years old—LWRHUs manufactured for the Cassini mission—are consistently

greater than expected, and it is unknown if this was due to the manufacturing process or a result of how the units were stored.

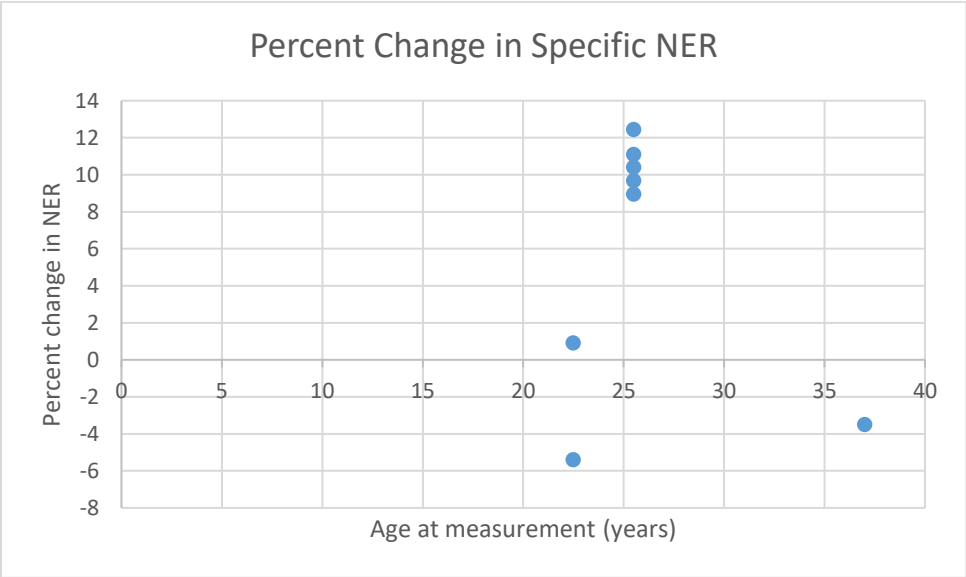

Figure 2. Percent change of NER per gram ^{238}Pu over time, showing deviation from the expected output from decay calculations.

Superimposing NER measurements from Mulford 2021 and freshly fabricated samples measured for PA-PQR-01022, *Process Qualification Report for HS-PuO2 Fuel Fabrication* in 2018, as seen in Figure 3, shows that new fuel has a higher specific NER, as would be expected, but different mission requirements might not lead to a direct comparison. Rather, the sample exchanged under normal atmosphere has a much higher NER and could provide a useful example for what the NER should look like if the reverse exchange occurred.

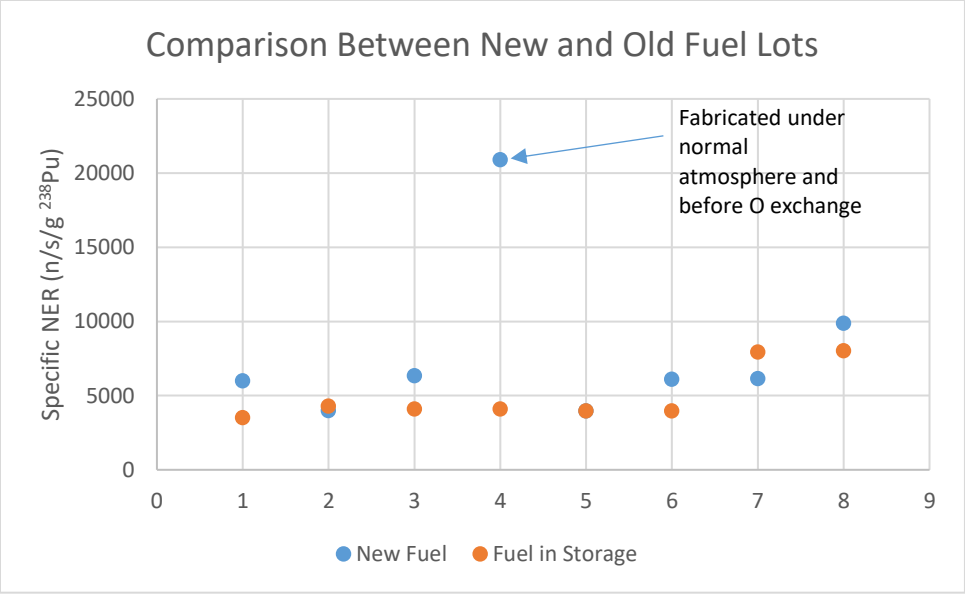

Figure 3. NER comparisons between new and older fuel. The x-axis values merely denote a sample and are not specific.

Pellet Impermeability

LWRHUs are fabricated by blending seasoned PuO_2 granules, with ^{18}O-^{16}O exchange and seasoning typically performed in several heating stages of 1000°C and 1600°C. The seasoning stages are usually for 25 hours, followed by a 6-hour soak at the respective temperatures in flowing argon saturated with $H_2{}^{16}O$ to reduce the NER below the required limit and then hot pressed. Hot pressing reduces the plutonia stoichiometry. Pellets are re-oxidized during the sintering process. Sintering is also performed under a saturated Ar-$H_2{}^{16}O$ atmosphere; after 6 hours at 1000°C and 6 hours at 1527°C, the pellet densities are increased (Rinehart 1988 & 1996, PA-PQR-01022). It has been shown that granule size does not have an effect on exchange, and that larger pellets have the same rate of exchange as smaller ones (Miles 1972). However, it was shown that highly dense refractory oxide does not undergo complete exchange and that sintering the pellet has an effect on the exchange rate (Deaton 1972). Pellets that were sintered at or above exchange temperatures did not experience complete exchange. For example, a pellet sintered at 1300°C will have limited exchange at 700°C and pellets sintered at 1600°C have little exchange at 700°C and higher yet still incomplete exchange at 1400°C.

Sintered pellets were also exposed directly to the atmosphere. At ambient temperatures, one sample had very little exchange. Another sintered sample was held at 200°C, and after a month of exposure underwent complete re-exchange (Miles 1972). These experimental observations are consistent with the LWRHUs in storage at LANL that have been measured. Both the Galileo and Cassini LWRHUs contain granules that were were hot pressed at 1100°C (60 wt%) and 1600°C (40 wt%) but the Cassini LWRHUs were sintered with <210 micron granules while the Galileo LWRHUs were sintered with <125 micron granules (Rinehart 1984 & 1996). As LWRHUs are sintered to between 75% and 90% TD (typically ~84% is the desired density), future experiments and measurements can include examining the microstructure of pellets sintered at various temperatures and granule sizes as well as measuring NER for pellets stored at different temperatures.

Exchange Kinetics

LANL currently has over 10 LHRWUs remaining from the Galileo mission, about 50 from Cassini, and over 10 others manufactured post-Cassini, with the almost 60 from Galileo and Cassini designated as flight-quality. For the units not used in missions, 6 LWRHUs are stored in a product can in a circular configuration around the perimeter of the can, with each LWRHU still in its aeroshell. Figure 4 is a thermal model of how a single LWRHU pellet is stored in a product can.

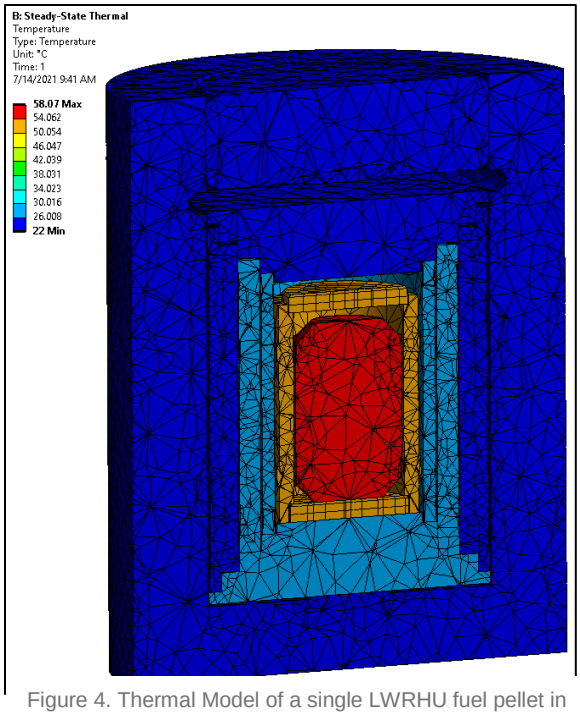

Figure 4. Thermal Model of a single LWRHU fuel pellet in a product can. Credit: Jon Teague, LANL E-1 Thermal and Mechanical Engineering

While this model shows that the outer temperature of a unit is about 55°C, older units are colder as there is less decay heat from the reduced amount of ^{238}Pu. Conversely, storage in proximity increases the temperature of the units. A thermal model that accounts for all six units in a product can needs to be made to precisely determine the storage temperature. Presently, it will be assumed that 55°C is reasonable temperature for new units, while the Galileo and Cassini LWRHUs drop to about 45°C. Both of these are well below the threshold for observable exchange, which is a storage temperature of 200°C (Miles 1972). Therefore, the reaction mechanisms driving the oxygen exchange at lower temperatures need to be investigated.

At high exchange temperatures, the predominant mechanisms are surface mobility, surface exchange, and internal chemical reactions (Winter 1968, Whiting 2015). It is also important to investigate the migration of point defects, and particularly oxygen migration. At all temperatures, the PuO_2 microstructure is dominated by oxygen as expected as the much larger and more highly charged plutonium atom is bound to its location on a face-centered cubic structure by comparison. The [100] direction vacancies have a lower energy barrier than [110] interstitial migrations (Wang et al. 2019) as shown in Table 1. Thus, at lower temperatures it is assumed that oxygen exchange will be due to oxygen migration from [100] vacancies.

At low temperatures, it would appear that the internal chemical reaction is the driving force for oxygen diffusion and exchange. Figure 5 is an Arrhenius plot of the different mechanisms from Whiting et al. At roughly 950°C, the internal chemical reaction becomes more prominent than surface mobility. Below 500°C, the exchange rate can be influenced by oxygen vacancies, where the exchange is simple heteroexchange. This exchange is defined as an isotopic exchange that swaps one oxygen from the solid oxide and one oxygen from the gas phase. The rate of these has not yet been experimentally determined for lower temperatures and has been done primarily for surface exchange rather than the bulk of a dense pellet. Peterson et al. provides excellent images of the microstructure of a plutonium oxide sample after experiencing temperature transients, depicting helium bubble growth along grain boundaries. Below 885°C, helium diffuses to the grain boundary faster than along it, leading to it being trapped at interstitial regions. As this study was done for helium at relatively high temperatures, it is indeterminate if it is applicable to oxygen.

Table 1. Activation Energies of Oxygen Migration Pathways or Mechanisms

Oxygen Exchange Reaction[1]		
Exchange Mechanism		Activation Energy (kJ/mol)
Internal Chemical Reaction		17.9 ± 0.9
Surface Mobility		35.3 ± 2.3
Surface Exchange		-
Point Defect Migration[2]		
Point Defect	Pathway	Activation Energy (kJ/mol)
O Vacancy	100	29.9
	110	359.9
	111	377.3
O Interstitial	111	128.3

[1]Data obtained from Whiting et al.
[2]Data obtained from Wang et al.

It is unclear whether or not the surface exchange or competing mechanism has any role to play at lower temperatures, especially for the interior of the LWRHU pellet. For sintered pellets, the decrease of specific surface area (SSA) further lowers the exchange rate of the surface based mechanisms (Deaton 1972). The bottom half of Figure 5 demonstrates the need for experimental results at lower temperatures. Based on a logarithmic extrapolation, the internal chemical reaction rate drops to zero at about 410°C and the surface mobility does as well at about 615°C, neither of which are realistic. There is information about point defect migration, but due to the pellet density, the mechanism of oxygen migration into the pellet is likely more energetically feasible by bulk defects, such as grain boundaries, rather than intrinsic point defects (Ando et al. 1976 and Peterson et al. 1984). At ambient temperatures and temperatures below 900°C, helium bubbles do not cause damage to the oxide microstructure, and that helium is trapped in structural defects (Land 1980). The coalescence of defects creates pathways and channels into the bulk of the pellet.

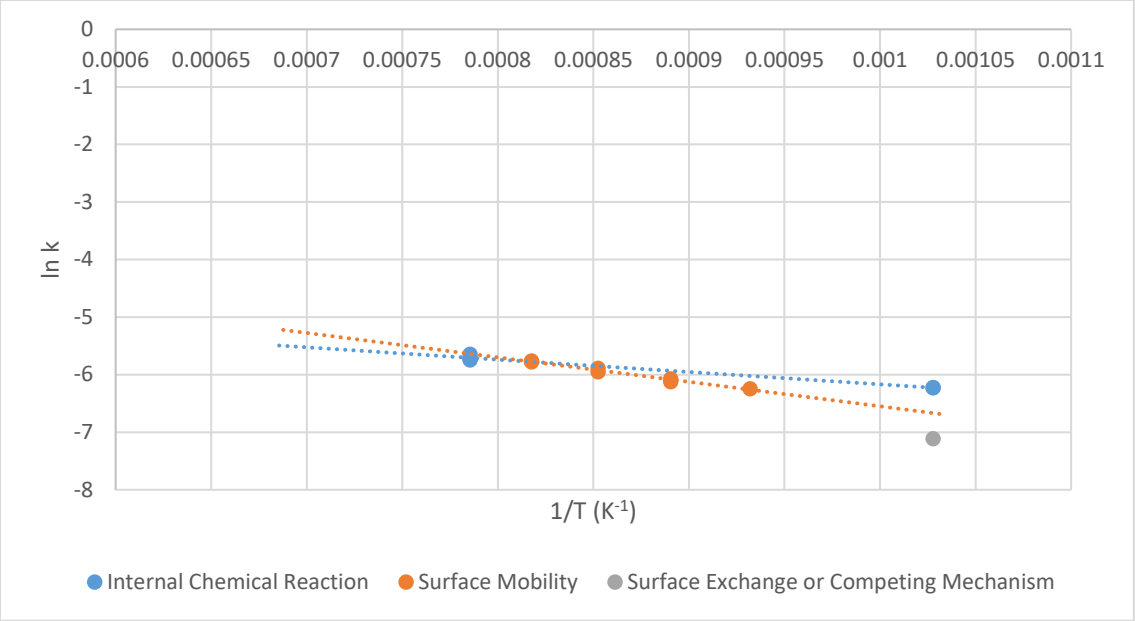

Figure 5. Arrhenius plot of Temperature and Reaction Rate using information from Whiting et al.

Using the natural logarithm of the Arrhenius equation, the rate and pre-exponential factor can be determined:

$$lnk = -\frac{E_a}{R_t}\frac{1}{T} + lnA$$

The surface mobility equation is estimated to be

$$lnk = -\frac{4245.9}{T} - 2.301$$

With the activation energy and pre-exponential factor known, the rates can be computed for a given temperature. The surface mobility rate at 200°C is 1.27 x 10^{-5} s^{-1}, and at a typical storage temperature of 50°C the rate is 1.97 x 10^{-7} s^{-1}. The diffusion coefficient calculated in Wang et al. for a substoichiometric ratio of $PuO_{1.998}$ at 300°C is 4.54 x 10^{-16} m^2/s, and will be slower for stoichiometric plutonium oxide due to less oxygen vacancies. The internal chemical reaction was not calculated as it is not a diffusion or surface based mechanism, and is postulated to be an activation mechanism (Whiting 2015).

Conclusions

NER is expected to increase over time as ^{18}O that was removed from the manufacturing process returns to equilibrium with atmospheric quantities while the LWRHUs are in storage. The only units that show consistency in back exchange were the Cassini units, showing an increase of between 9% and 12.5%. The most likely factor restricting back exchange is pellet impermeability. Studies have shown that high density metals and oxides have little to no exchange (Deaton 1972 and Miles 1972). Furthermore, sintering the pellet reduces the availability of surface exchange mechanisms due to the increased density and reduced specific surface area. Because manufacturing variations dominate NER measurements, the temperatures and granule sizes used in hot-pressing have a role in oxygen exchange. The higher the temperature a pellet is sintered at, the less ^{18}O is back exchanged over time. The Galileo, Cassini, and post-Cassini LWRHUs use the same seasoning process. However, the Cassini LWRHUs were sintered

using larger granules (<210 microns) than the Galileo units (<125 microns). The effects of the size of granules used for sintering needs to be studied further, but it has been reported that smaller grain sizes inhibit the formation of grain-boundary gas bubbles (McDonell 1975).

There is hardly any literature on low temperature oxygen exchange in PuO_2. The reported information consists of heteroexchange being dominant at surfaces when the temperature is less than 500°C and that very little exchange occurs below 200°C. The experiment that yielded no observable exchange rates of PuO_2 pellets stored at sub-200°C temperatures was conducted over the course of several weeks and is consistent with the Cassini LWRHUs that were in storage for more than two decades. LWRHUs in storage are not expected to have surface temperatures exceeding 60°C. At this temperature and below, the internal chemical reaction is dominant due to not needing a high temperature surface as well as the elevated temperatures near the center of the pellet driving a higher rate of diffusion. The primary diffusion mechanism into the pellet is caused by intrinsic point defects utilizing oxygen vacancies in the fluorite lattice. This mechanism is in agreement with the data obtained for oxygen diffusion in thorium oxide as well as helium released from plutonium oxide (Ando 1976, Peterson 1984). The lower energy pathway is calculated to have an activation energy of 29.9 kJ/mol (0.31 eV) (Wang 2019). The migration of this defect into the lattice is expected to be very slow at lower temperatures, as few oxygen molecules in air have the threshold energy at or slightly above room temperature.

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